

Achieving a 10,000 GPU Permeance for Post-Combustion Carbon Capture with RTIL-based Membranes

2011 DOE NETL CO₂ Capture Technology Meeting

Pittsburg, PA

Aug 22, 2011



Objectives

- **Design mechanically and chemically robust room temperature ionic liquid (RTIL)-based selective layers (SLs) having CO₂ permeability exceeding 1000 barrer and a CO₂/N₂ selectivity of at least 20.**
- **Develop ultrasonic atomization based coating technique to fabricate less than 100 nm thick selective layer/microporous support composites.**
- **Devise technically and economically viable membrane performance characteristics and process scenarios for CO₂ capture from coal derived flue gas.**
- **Achieve 10,000 GPU membrane permeance & selectivity > 20**

Approach

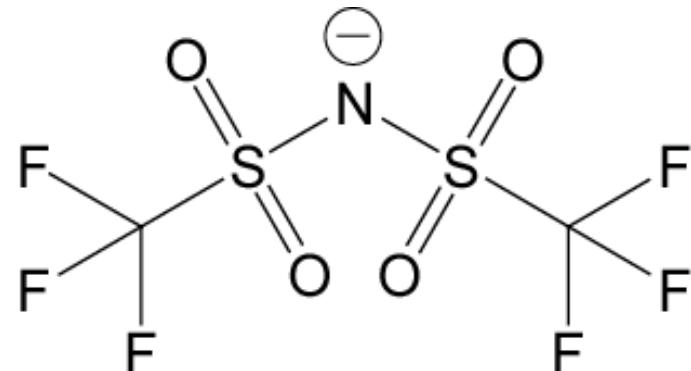
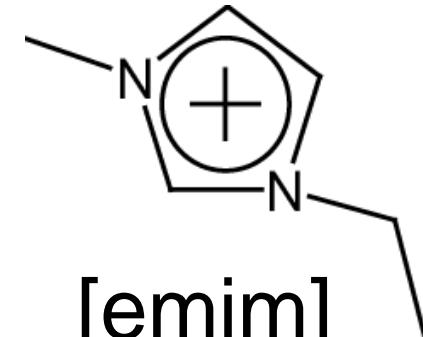
- **Selective Layer Design Synthesis & Evaluation**
 - **Tailored gel-RTILs, RTIL/Poly(RTIL) composites, incorporation of task-specific CO₂ complexation chemistries**
- **Ultra-Thin Membrane Fabrication, Optimization, & Testing**
 - **Commercially viable fabrication technique development using ultrasonic spray-coating technology (USCT) -- enables controlled ultra-thin SL deposition on commercially attractive support platforms**
- **Membrane, Systems, and Economic Analyses**

Ionic Liquids



Imidazolium-based Room Temperature Ionic Liquids (RTILs)

- Organic salts
- Become liquid at or below 100 °C
- Non-flammable
- Negligible vapor pressure
- Thermally stable above 200°C
- Polymerizable versions
- High CO₂ solubility
 - Good CO₂/N₂ solubility selectivity



[Tf₂N⁻]

Henry's Constants (H) of CO₂, CH₄, and N₂ at 40 °C

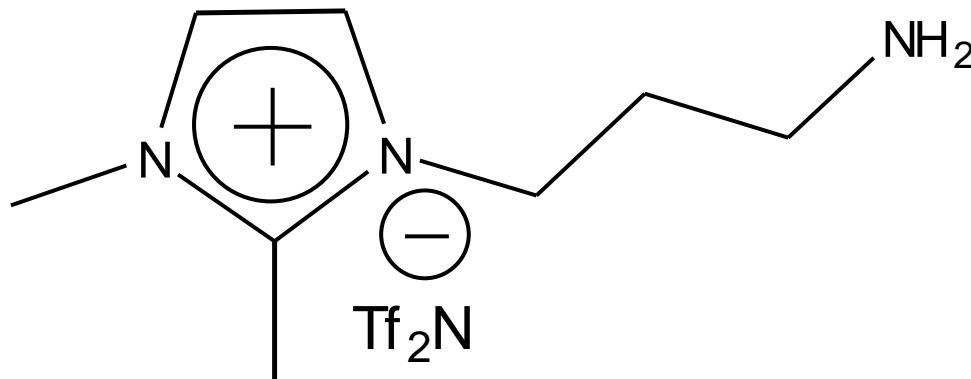
$$\alpha = 25$$

RTILs	CO ₂	CH ₄	N ₂
[emim][dca]	95	2000	4800
[emim][Tf ₂ N]	46	550	1160
[emim][CF ₃ SO ₃]	71	1200	2700
[hmim][Tf ₂ N]	40	352	940

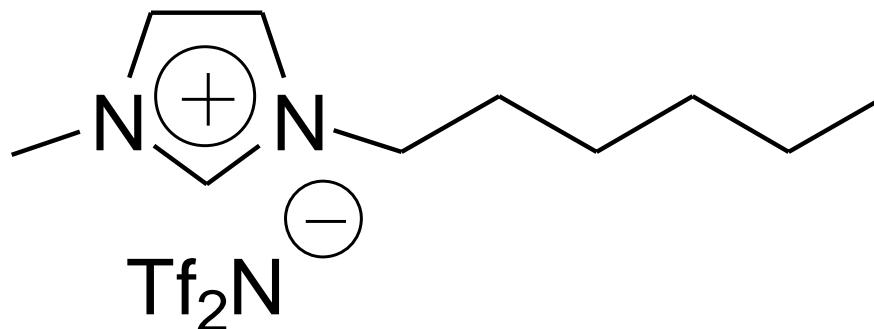
Amine Functionalized RTILs & RTILs with Free Amines



Amine Functionalized RTIL/RTIL Mixture

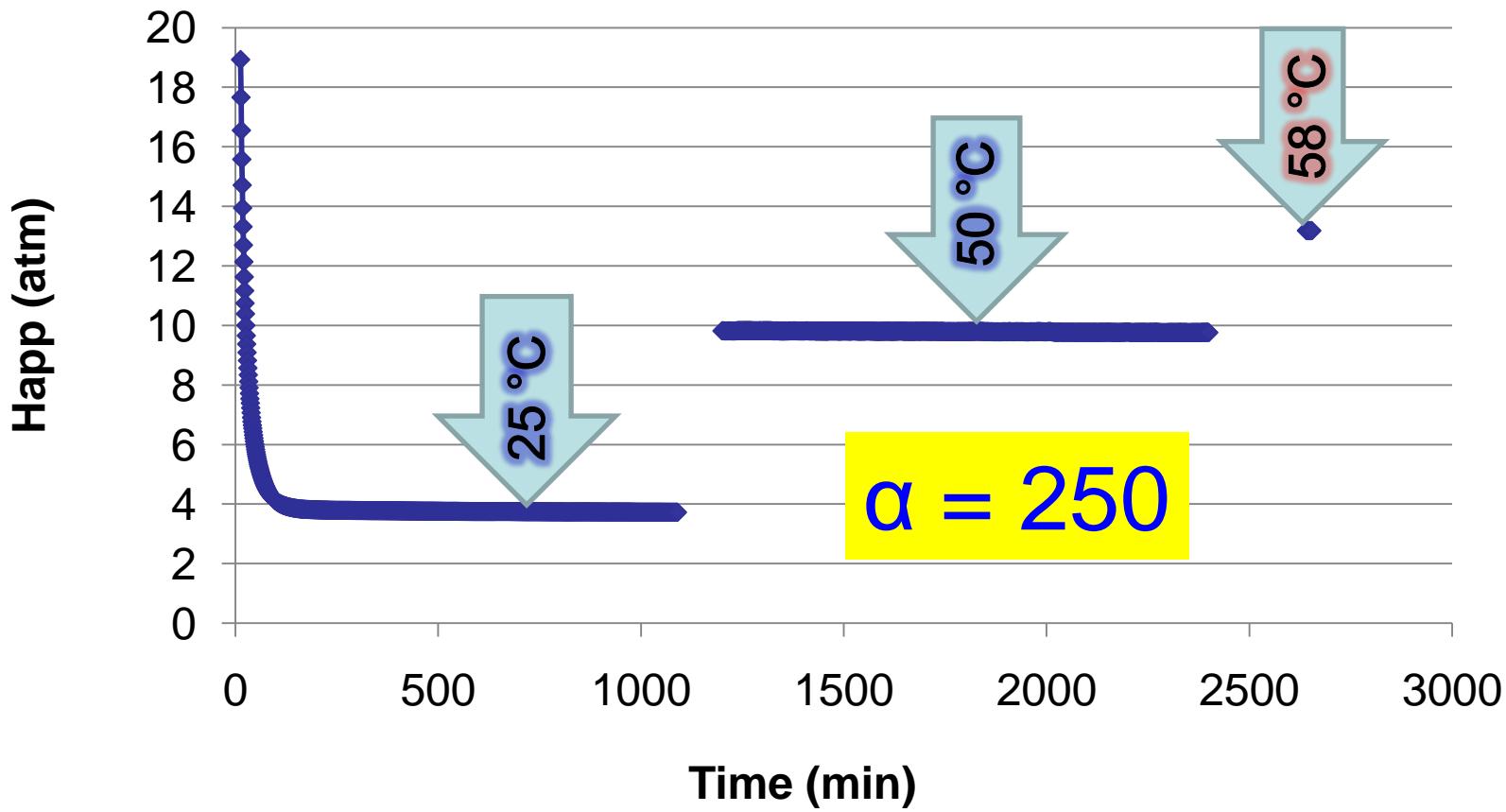


$\text{NH}_2(\text{CH}_2)_3\text{ mmim Tf}_2\text{N}$

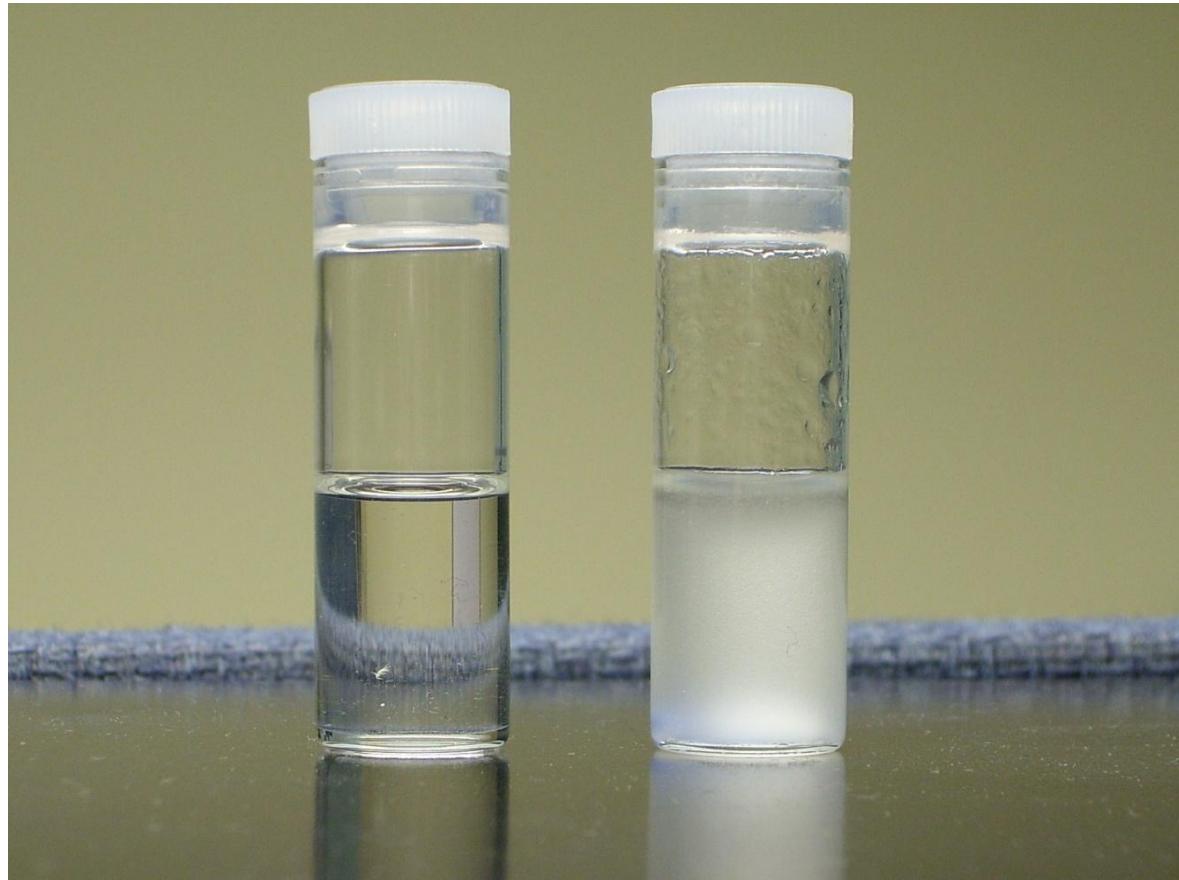


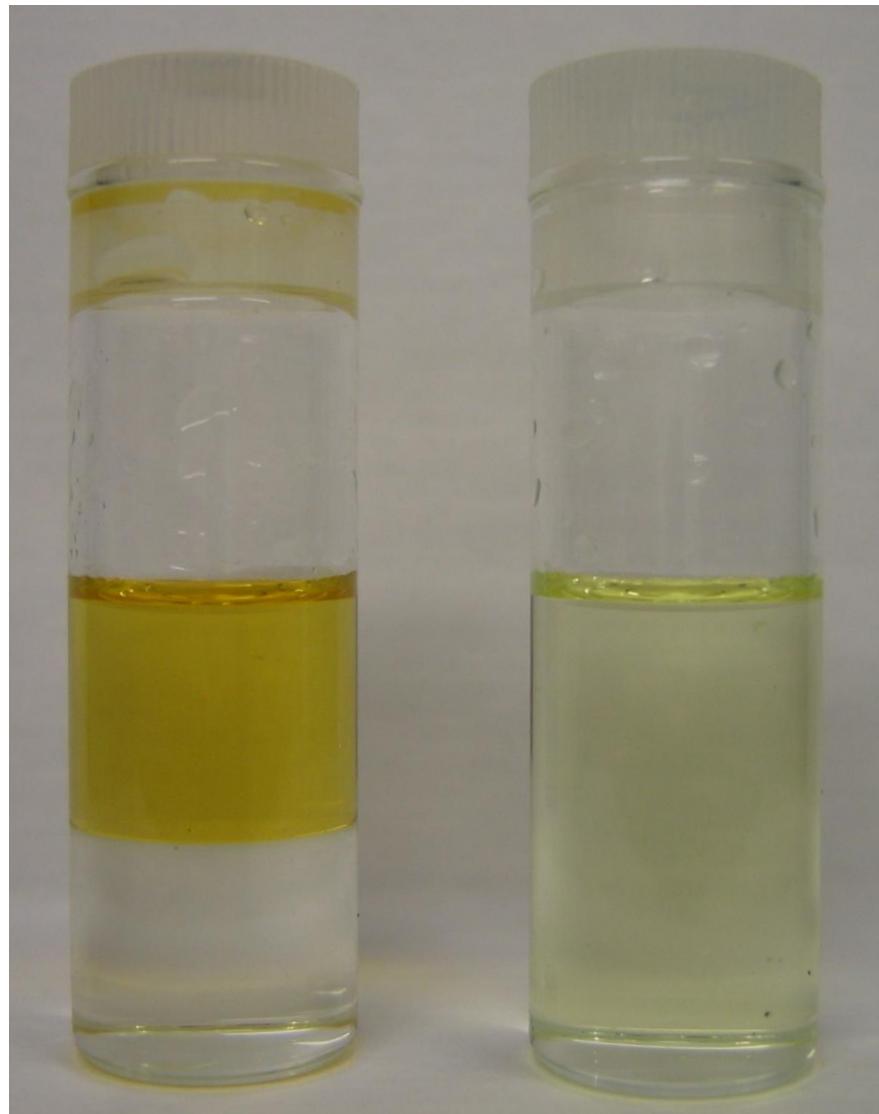
$\text{hmim Tf}_2\text{N}$

**65.5 mole % [hmmim] [Tf₂N]/34.5 mole%
[NH₂(CH₂)₃mmim][Tf₂N]**



CO₂ Unloaded vs Loaded for a 50/50 mole % Mixture of MEA/[hmim][Tf₂N]



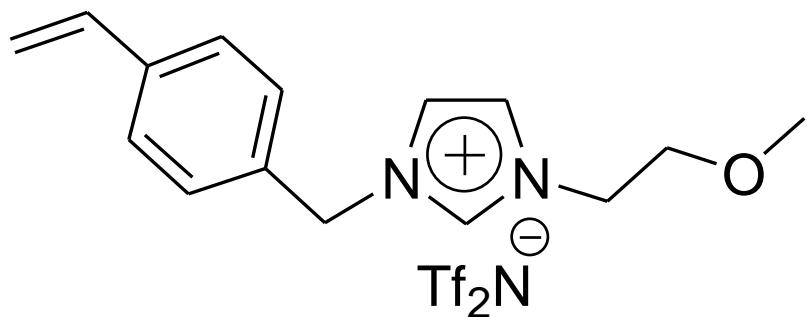


Morphologies



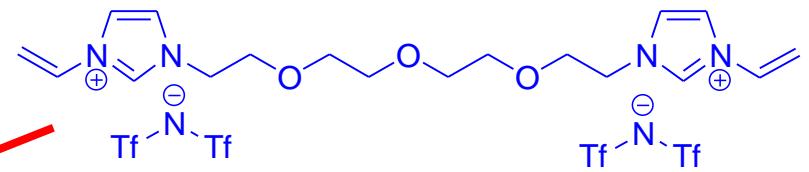
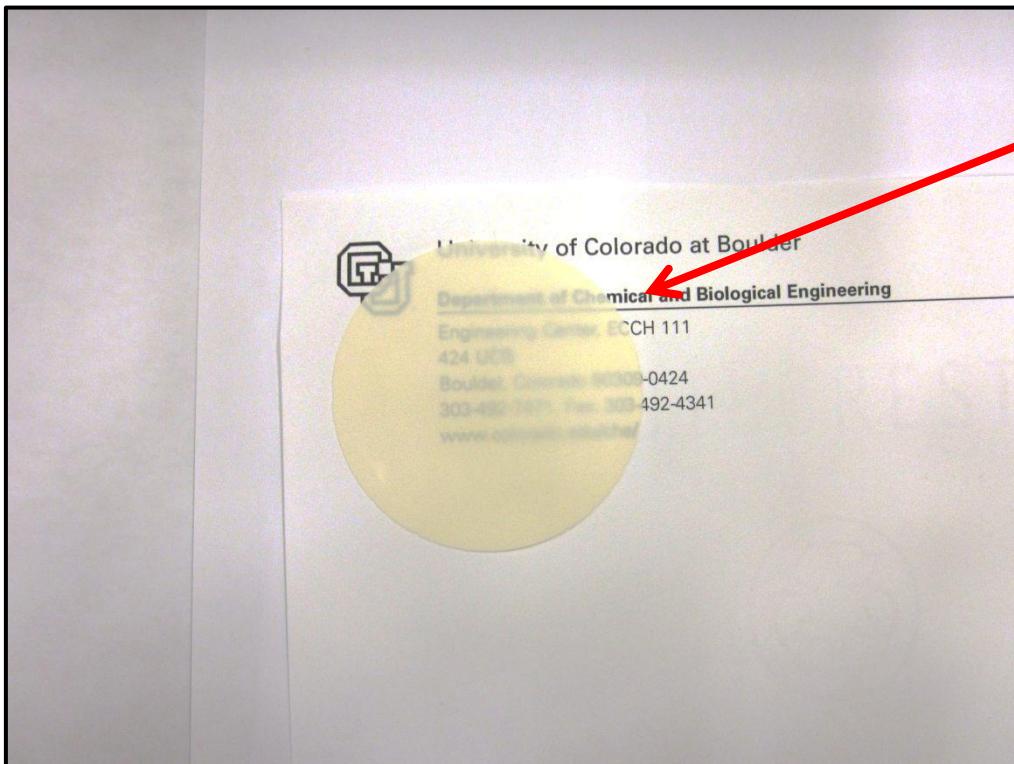
Polymerized RTILs

- RTILs can also be readily functionalized with polymerizable units



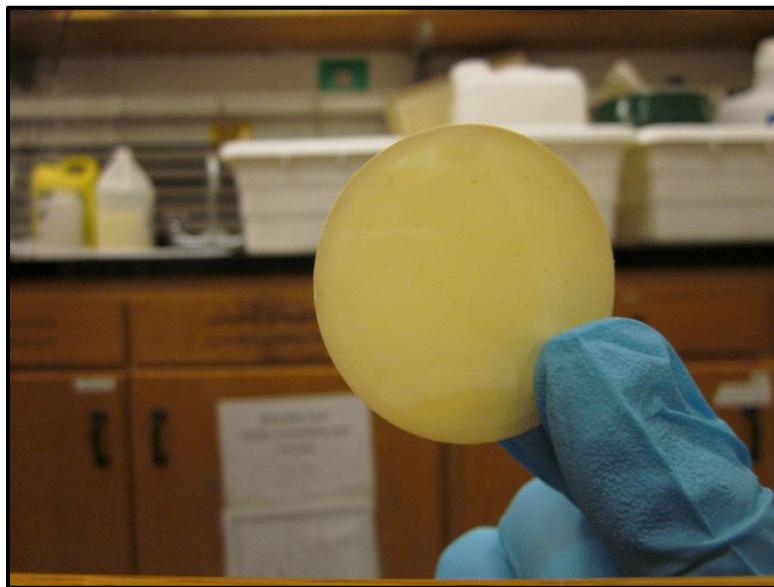
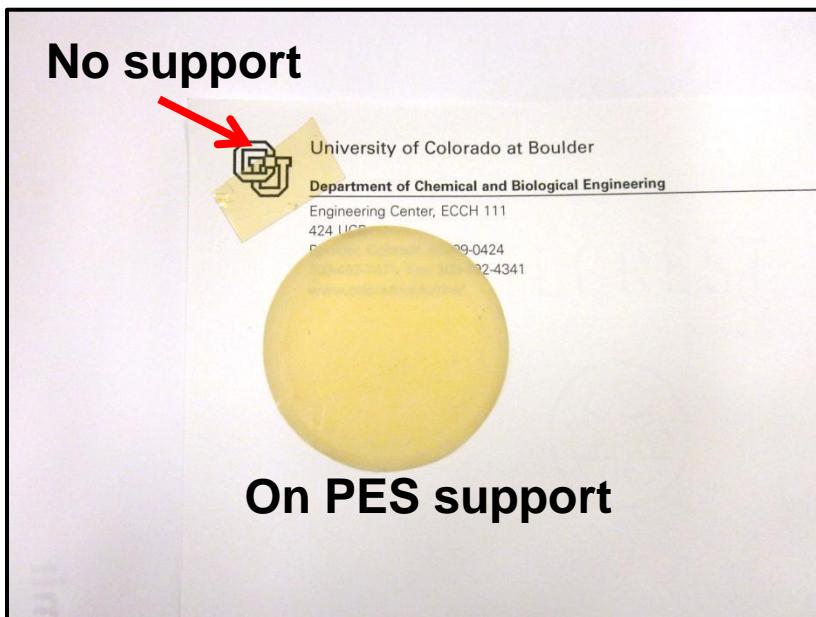
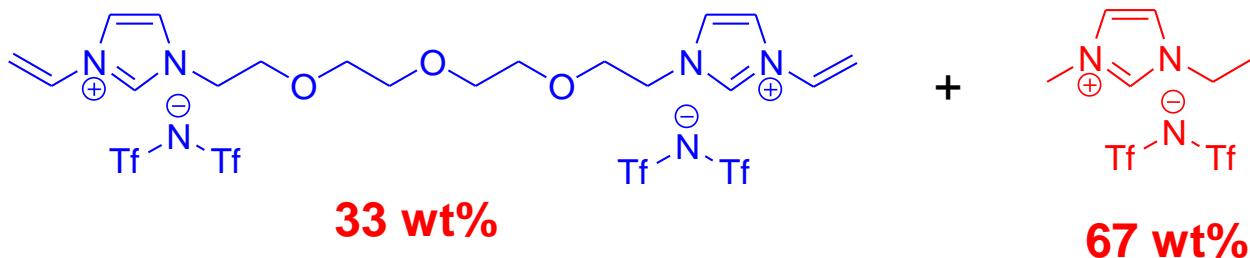
- Can form dense, solid poly(RTILs): a new class of polymers with unique and tunable properties

Neat polymerized RTIL – no free RTIL

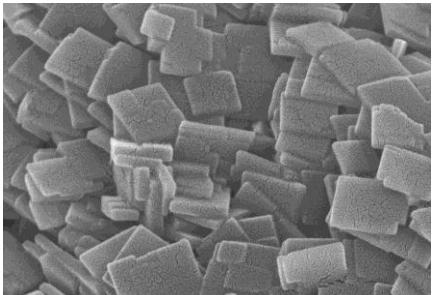


- Gemini vinylimidzolium
- PES support

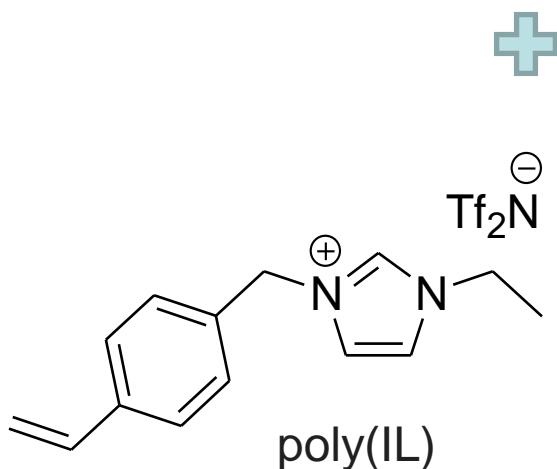
Polymerizable RTIL + free RTIL



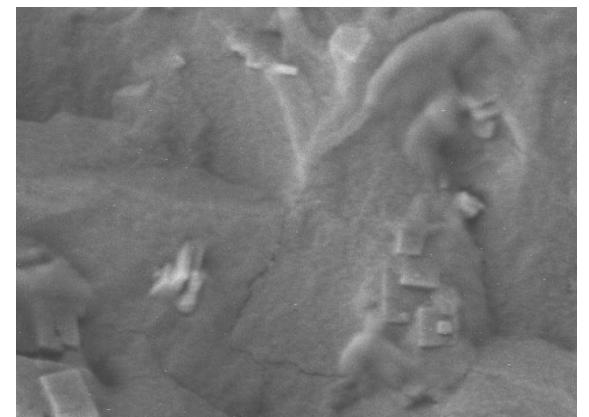
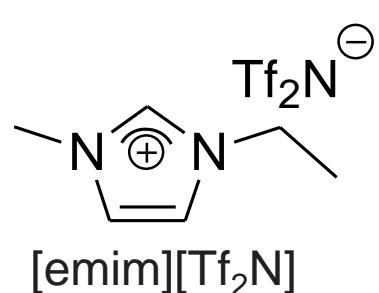
Fabrication of SAPO – 34 – Poly(IL) Composite Membranes



SAPO-34 100 nm



UV light
crosslinker

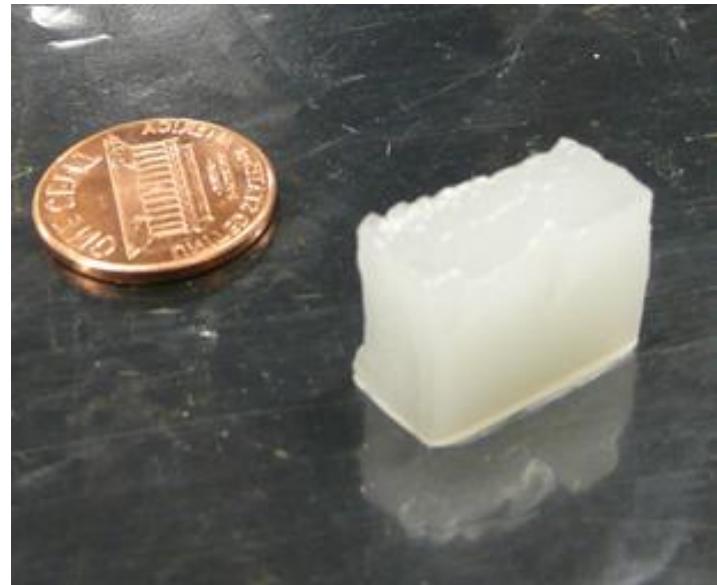


10 wt% of SAPO-34 &
(80-20)wt% of styrene poly(IL) and
[emim][Tf₂N] composite membrane

Gels: Solid Networks

□ Physical Gel

- physically bonded network
 - hydrogen bonding, van der Waals interactions, and π - π bond stacking
- sol-gel thermal transition



Membranes



Membrane Terminology

Flux = moles/(surface area · time) = J

$$J = \frac{(D \cdot S) \Delta P}{L}$$

Permeability = (D · S)

Permeance = (D · S) = Material Prop
L Thickness

Membrane Terminology

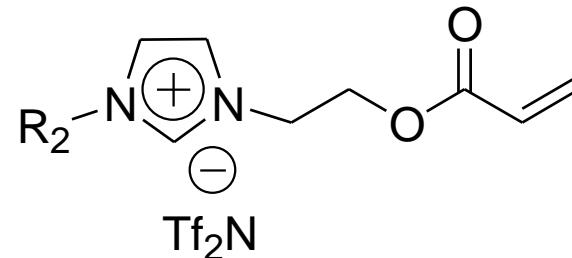
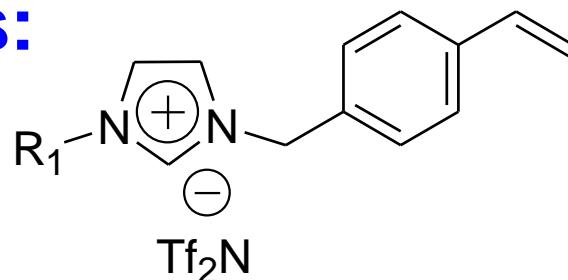
Permeability = $(D \cdot S)$ → Barrer

Permeance = $\frac{(D \cdot S)}{L}$ → GPU

10 Barrer/0.1 micron = 100 GPU

First-Generation Poly(RTIL) Gas Separation Membranes

- **Synthesize RTIL monomers of the following types in two or three simple steps:**



$\text{R}_1 = \text{Me, Bu, Hx}$

$\text{R}_2 = \text{Me, Bu}$

- **Polymerize into (lightly crosslinked) films**

Robeson Plot for CO₂/N₂

First generation
poly(RTIL)
membranes

CO₂ / N₂ Permselectivity

10.0
1.0

1 10 100 1000 10000 100000

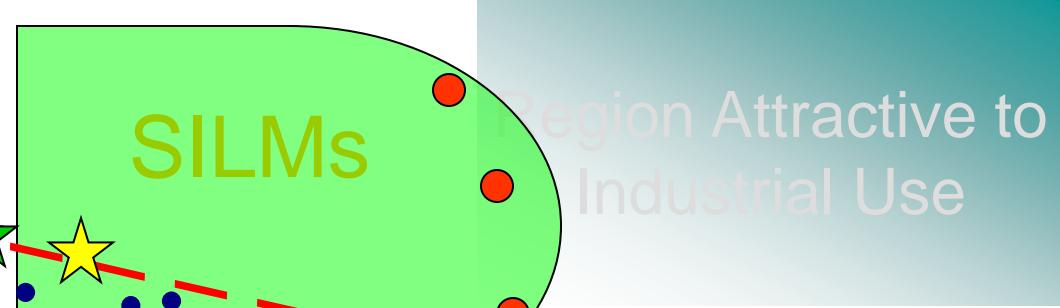
CO₂ Permeability (Barrers)



Styrene-based



Acrylate-based



Region Attractive to Industrial Use

“Flux selectivity trade-off”

Polymer membranes

SILMs

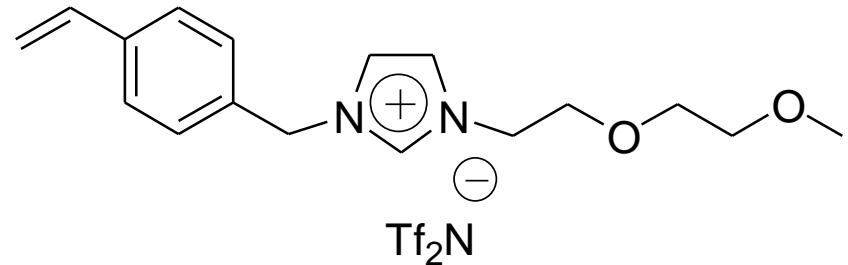
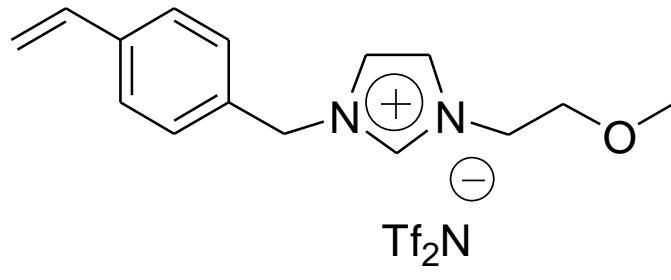
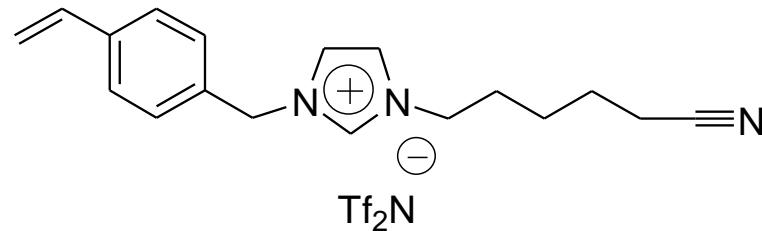
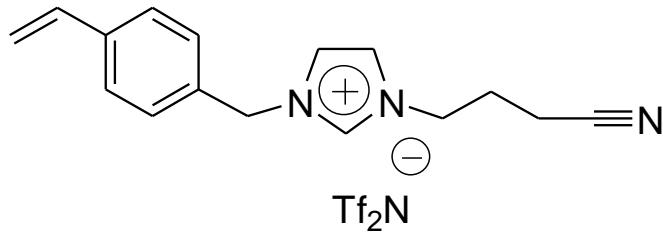


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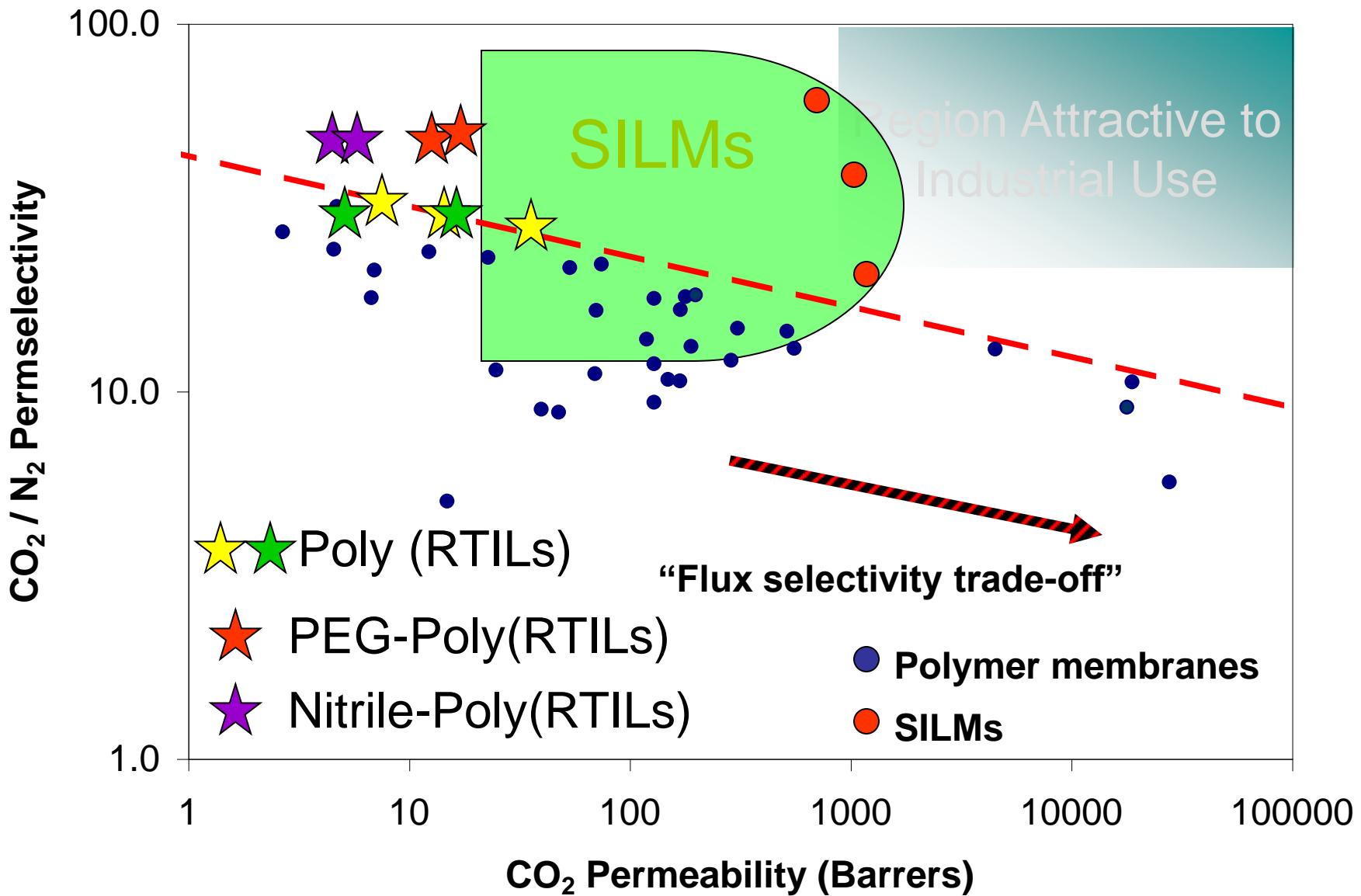


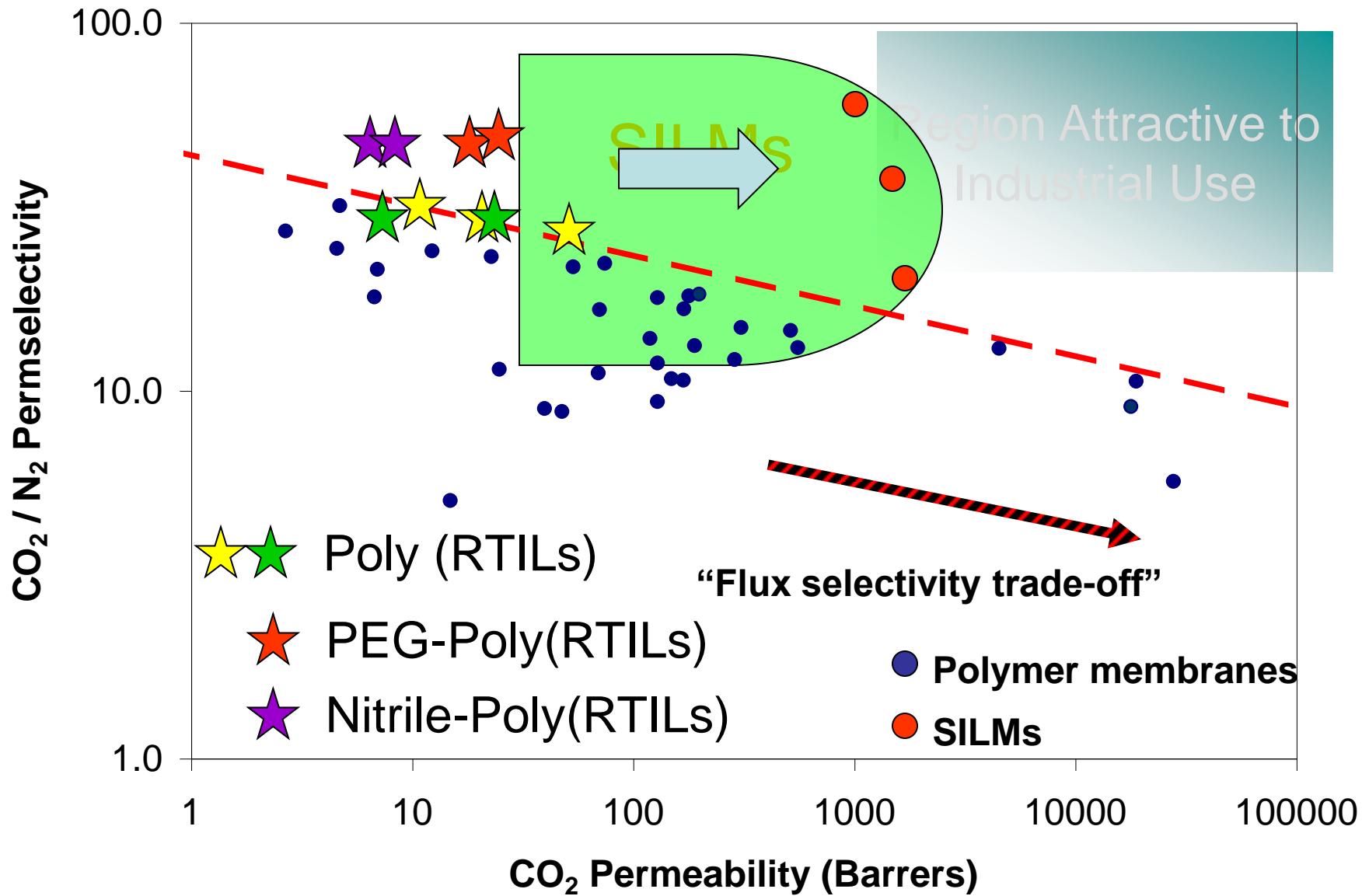
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Poly(RTILs) w/ Pendant Groups



Poly(RTILs) Above Upper Bound



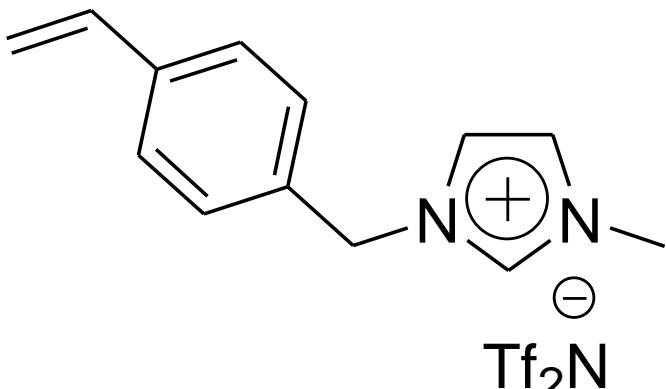


Composites

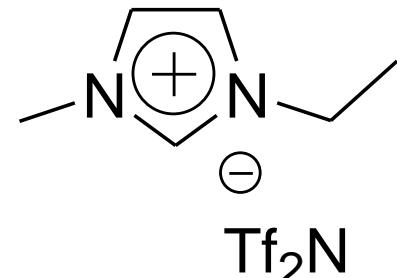


Polymer – RTIL Composites

- While poly(RTILs) have good CO₂ separation properties, they have low P (D).
- Combine polymerizable imidazolium salts w/ non-polymerizable RTILs to improve diffusion?

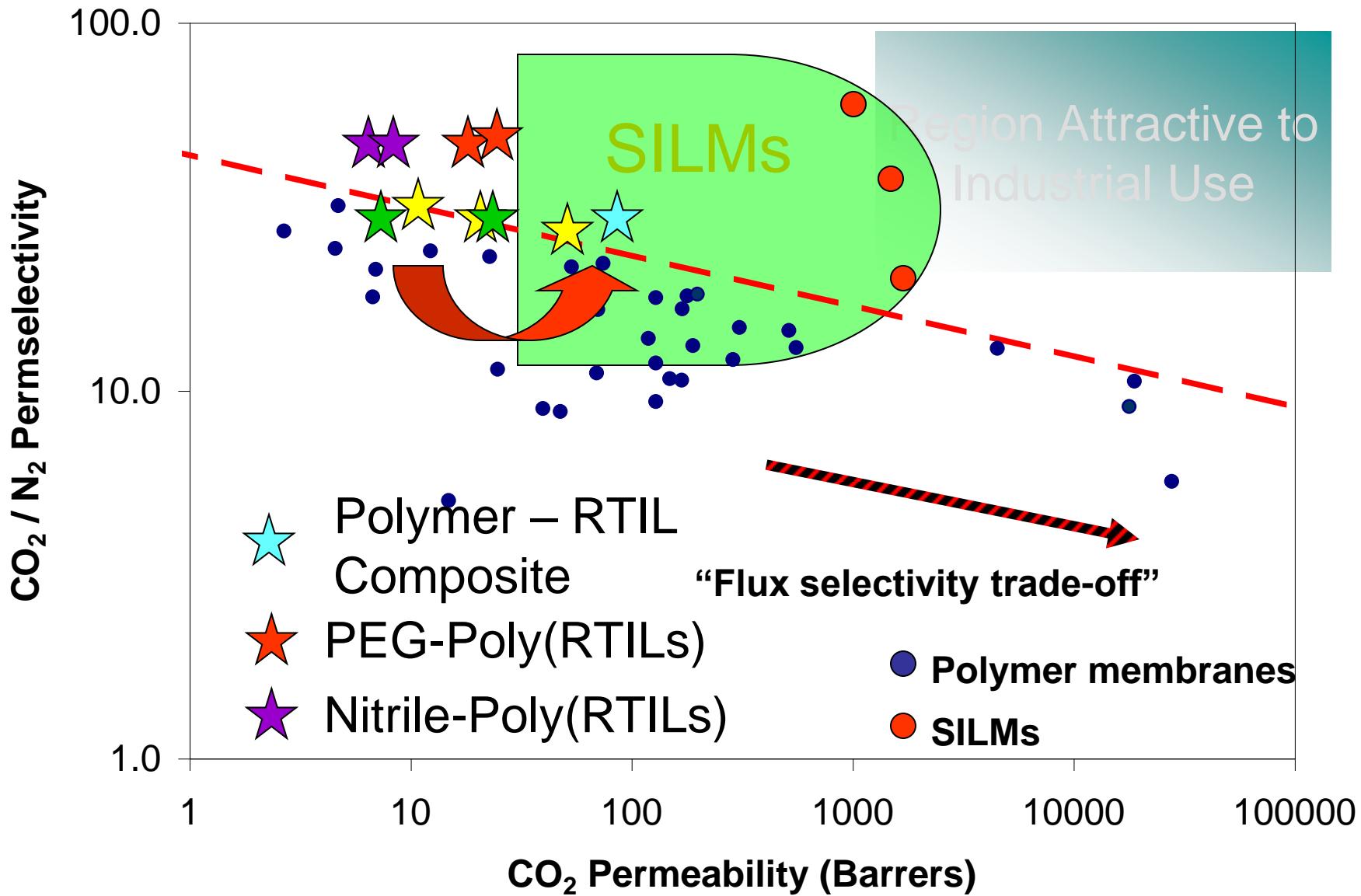


80%



20%

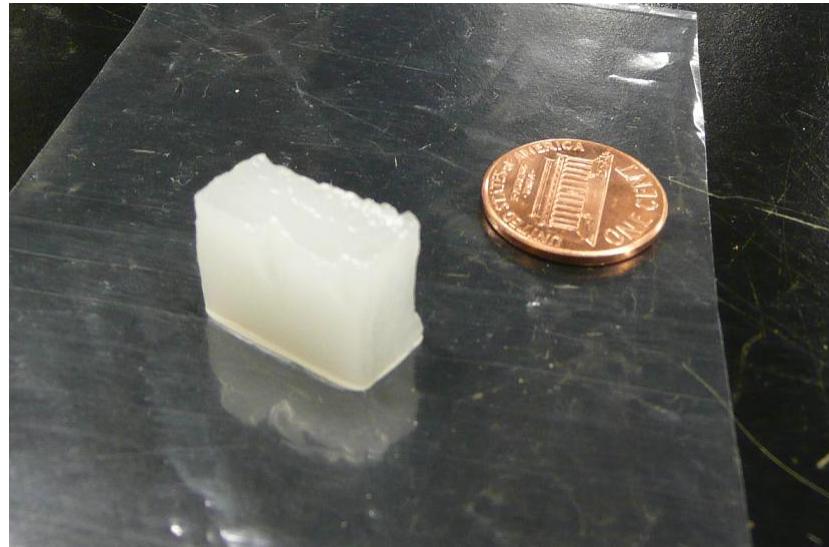
Improved Permeability



Proof of Concept System

Gel Membrane

- hmim/Tf₂N 98.5 wt%
- 12-hydroxy stearic acid 1.5 wt%
- 67 C melt temperature
- Supor membrane support



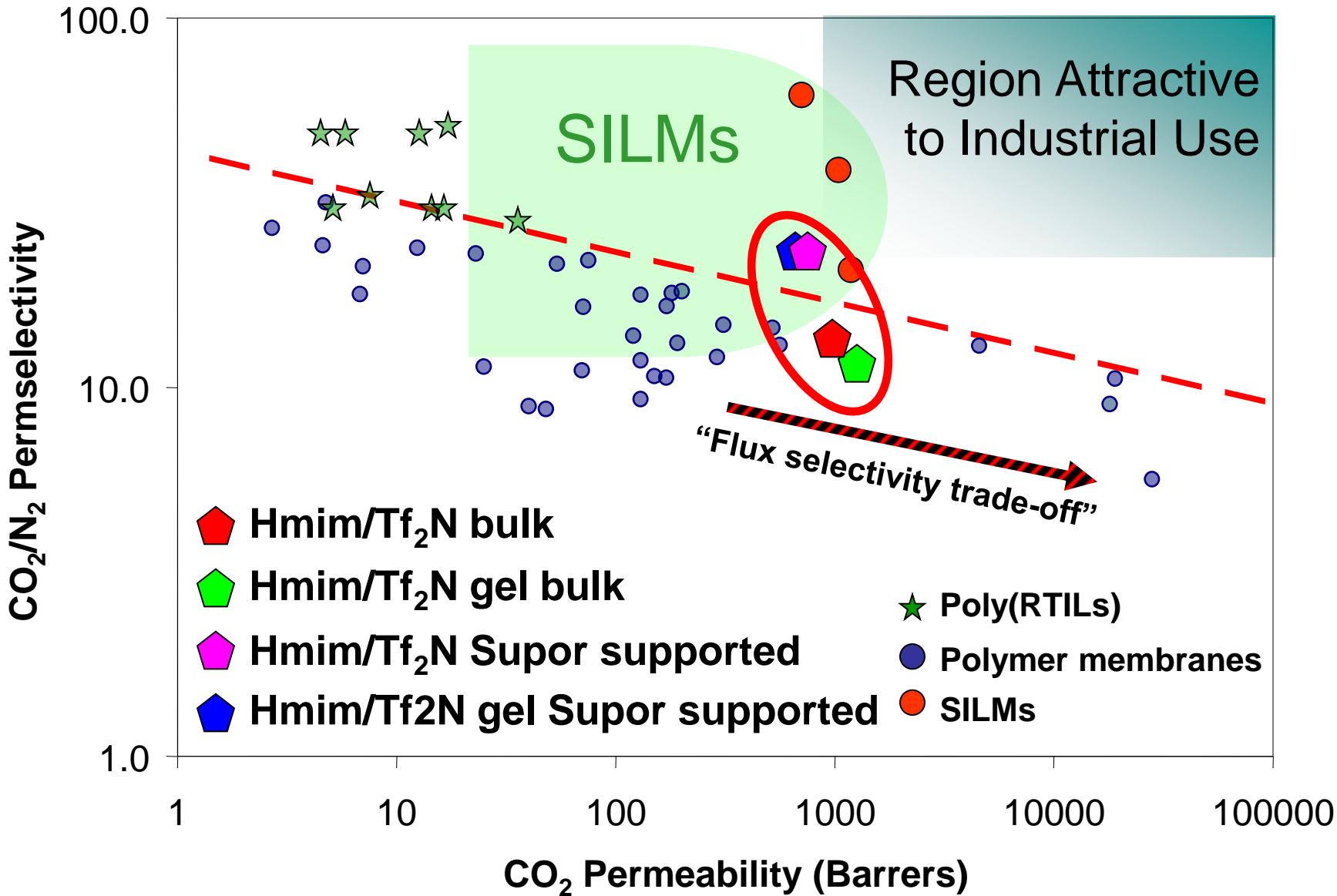
Gelled hmim/Tf₂N



gelled

neat

Gel Membranes: Liquid-Like Permeability



Membrane Terminology

Permeability = $(D \cdot S)$ → Barrer

Permeance = $\frac{(D \cdot S)}{L}$ → GPU

10 Barrer/0.1 micron = 100 GPU

(commercial polymer membrane)

1000 Barrer/0.1 micron = 10,000 GPU

(gel membrane)

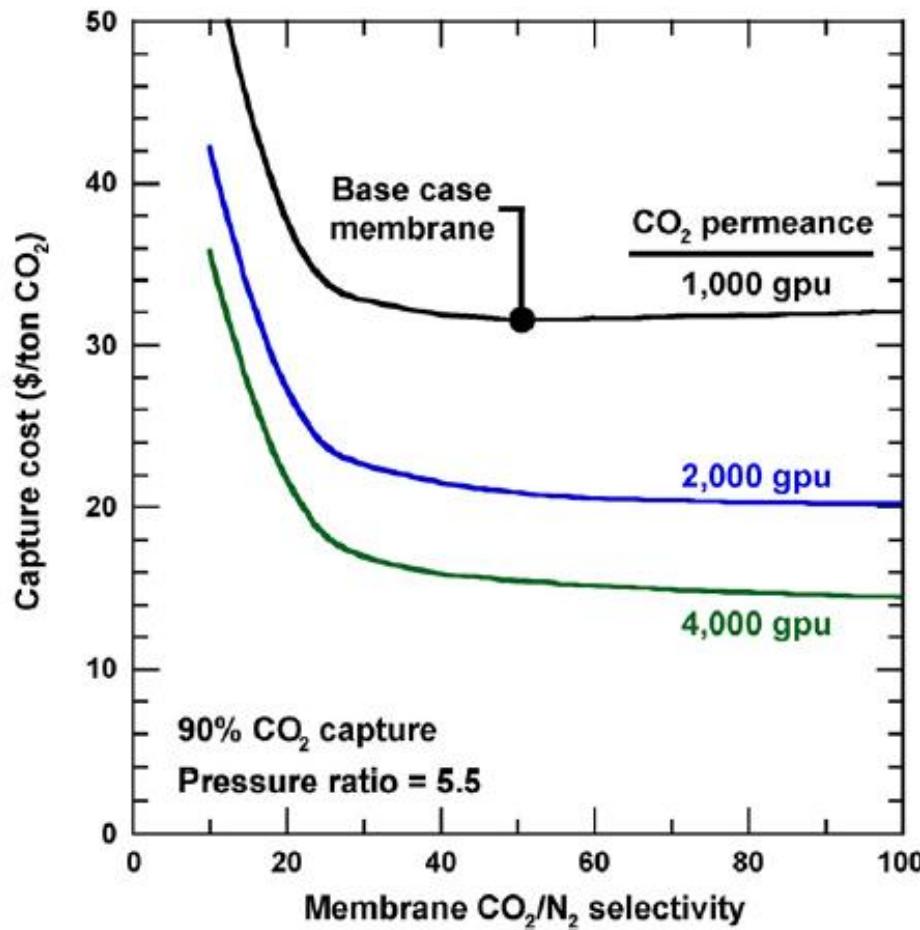
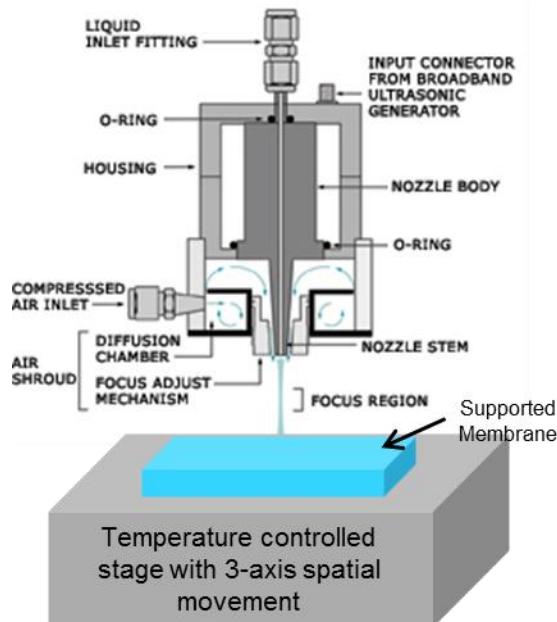


Figure 1: Effect of membrane CO₂/N₂ selectivity on the cost of capturing 90% of the CO₂ in flue gas for membranes with a CO₂ permeance of 1000, 2000, and 4000 gpu at a fixed pressure ratio of 5.5⁴

Ultrasonic Spray Coating Technique (USCT)

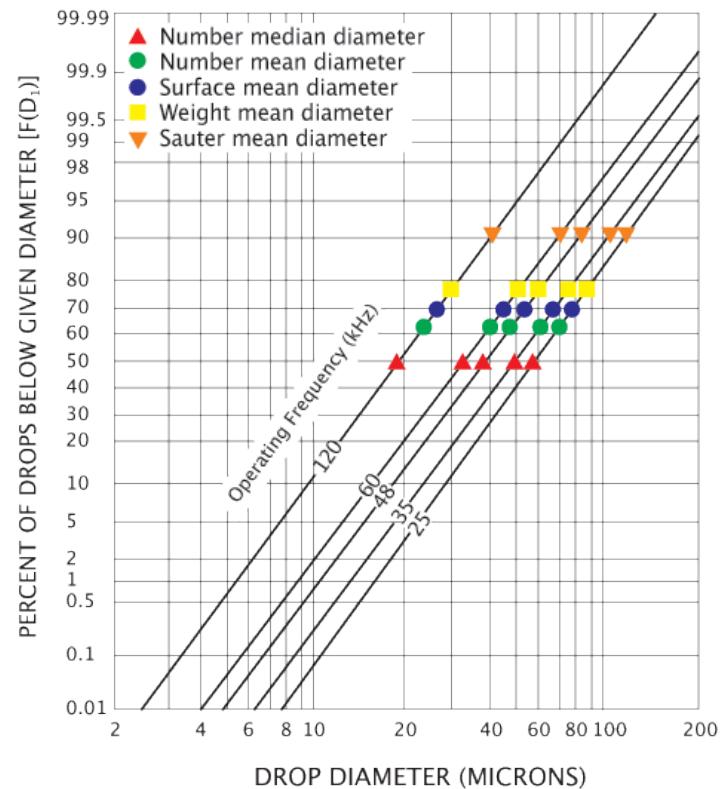
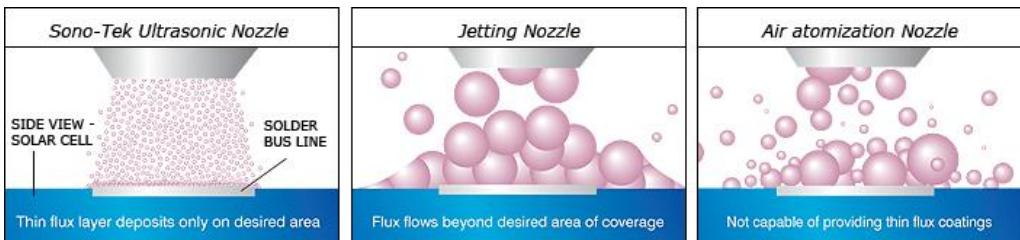
- Ultrasonic atomization based spray coating process to fabricate ultrathin gel-RTIL or RTIL/poly-RTIL composite membranes supported on micro-porous substrates.
 - Ultrasonic atomization using piezoelectric crystal
 - Proven technology for numerous industrial thin film coating applications, e.g. fuel cell, solar cell, food packaging
- Precisely controlled spray and deposition process facilitates ultrathin film formation with thickness in submicron range.



Source: www.sono-tek.com

Characteristics of Ultrasonic Atomization

- Atomization: Precise control on droplet size with narrow droplet size distribution.
- Soft spray profile reduces pore penetration in the porous support layer.
- Temperature control and dual feed options aid in controlled RTIL film formation.
- Minimal overspray

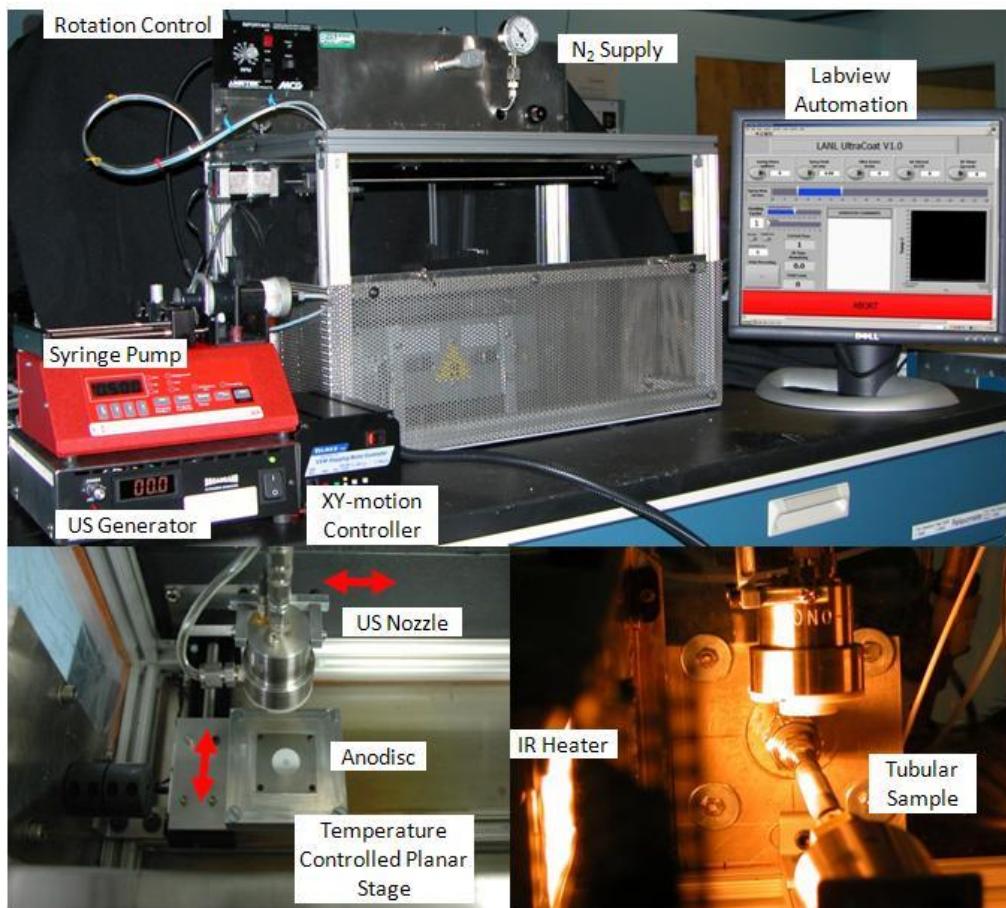


Note: Data compiled for water. Other materials may give different results.

Source: www.sono-tek.com

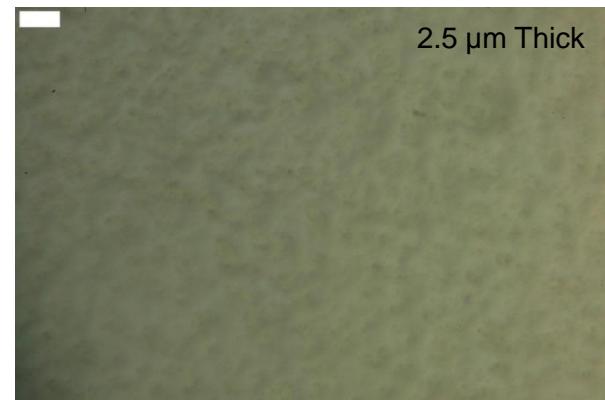
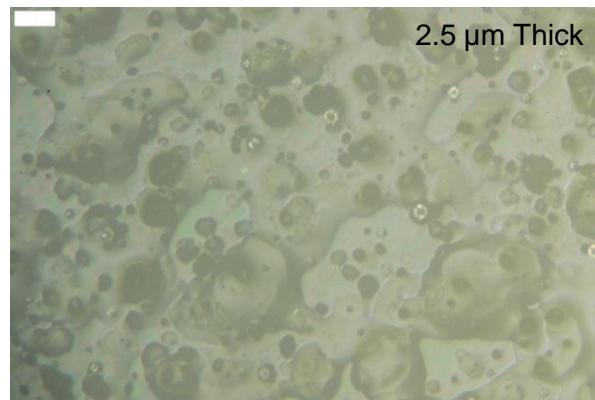
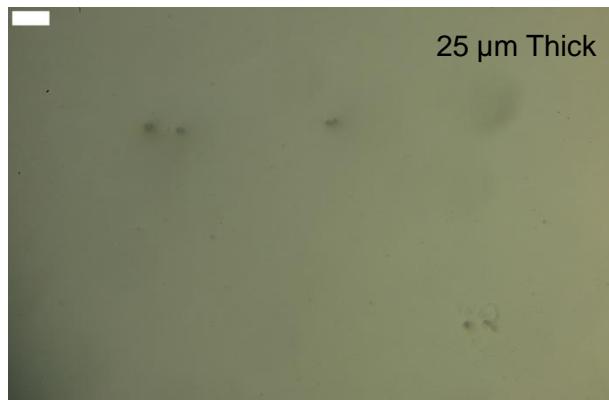
LANL USCT System

- **Semi-automated ultrasonic spray coating system for ultrathin film deposition.**
- **Self contained enclosure to control coating environments (image w/o cover).**
- **System control parameters include:**
 - Liquid flow rate
 - Spray profile
 - Raster speed
 - Substrate temperature
 - In-situ IR and UV irradiation
 - Labview® automation



Preliminary Gelled RTIL Coatings

- Preliminary spray coating experiments conducted with [emim][Tf₂N] solution on glass slide
- The morphology of coated layer is dependent on the spraying parameters
- A uniform film of gelled RTIL can be obtained via USCT
- Spray coating process optimization required to obtain smooth, defect free, uniform film with minimum pore penetration



Scale bar

Finish



The University of Colorado

